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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the visible photopolymerization nature constituent containing the compound in which cationic polymerization is possible, and it is especially related with improvement of the visible photopolymerization nature constituent with large exposure speed in a long wavelength region to which after photo-curing becomes near transparently and colorlessly further.

[0002]

[Description of the Prior Art]Many photopolymers and photoresist which used photopolymerization conventionally are known, and are used in various fields, such as a printing plate and manufacture of a semiconductor. In these photopolymerization nature constituent, a benzoin derivative, an aromatic quinone compound, an aromatic ketone compound, etc. have mainly been used as the polymerization initiator. By the way, when these photopolymerization initiators were used, since the exposure speed of a photopolymerization nature constituent was slow, it had a long time in the exposure in image formation. For this reason, the influence by the slight vibration under generation of heat generated by the great energy ray by long exposure or operation always needed to be taken into consideration. It also had the problem which is easy to produce deterioration of the constituent by heat. Although these photopolymerization initiators have photosensitivity in an ultraviolet region of 400 nm or less, they hardly show photosensitivity in the visible ray region of long wavelength from this. For this reason, the conventional photopolymerization nature constituent had a problem to which that use is limited remarkably.

[0003]On the other hand, in recent years, development of laser plate making, a printed circuit board, an optical disc, optical memory, a hologram, and the laser recording material for laser lithography is called for with progress of laser technique. And as a laser light source from

which a stable output is obtained now, there are argon, helium neon, YAG, a semiconductor laser, etc. However, it was difficult to apply the conventional photopolymerization nature constituent in which there is each oscillation wavelength of these light sources to what attains to infrared rays at not less than about 500 nm, and the above-mentioned photopolymerization initiator was contained to the above-mentioned laser recording material as it is. For this reason, development of the photopolymerization initiator which has high sensitivity to visible light is made briskly now. And in U.S. Pat. No. 2850445, it is reported that the photopolymerization nature constituent which added photoreduction nature colors, such as a rose bengal, eosine, or erythrosine, shows good visible light photosensitivity. As improvement art, the compound initiator system of a color and amine (refer to JP,44-20189,B), The system of hexaaryl biimidazole and a color (refer to JP,45-37377,B), the system (JP,47-2528,A.) of hexaaryl biimidazole and p-dialkylamino benzylikenetone Refer to JP,54-155292,A, the system of a 3-keto coumarin and an active halogen ghost (refer to JP,58-15503,A), The system of substitution triazine and merocyanine dye (refer to JP,54-151024,A), The system of coumarin series coloring matter and diaryliodonium salt (refer to JP,3-62162,B), The proposal of the system (refer to JP,3-55483,B) of a rhodanine derivative, the system (refer to JP,3-62164,B) of diaryliodonium salt and a porphyrin complex, and diaryliodonium salt, etc. has been made.

[0004]In order to prevent these colors from remaining to that by which originated in having used coloring matter, a color, etc. as a sensitizer, and coat formation was carried out, many proposals using cyanine dye as a sensitizer faded or decolorized are also made by the ability to irradiate with a light strong after coat formation. As such a proposal, the organic boron compound anion salt (refer to JP,62-143044,A, JP,64-13141,A, and JP,2-3052,A) of organic cationic dye is reported. The not a form but system (refer to JP,2-4804,A and JP,5-194619,A) added separately of the complex are also proposed in the organic cationic color and the boron acid salt as improvement art from use of a broad color, and a viewpoint of facilitation of operativity.

[0005]

[Problem(s) to be Solved by the Invention]By the way, although it can be satisfied with the sensitization field and the field of operativity of the photopolymerization nature constituent for these laser recording materials of the former proposed as mentioned above, it was not yet enough about the color resulting from the coloring matter in which the field of exposure speed and a hardened material remain.

[0006]For this reason, in photography of the hologram etc. which have a problem which cannot aim at large shortening of exposure time, and are easy to be influenced by vibration under exposure, it had a problem for which it is not suitable. When it was considered as the method of lamination at the resin board of the same presentation, or the resin board of another

presentation, stiffening a resin board which absorbs ultraviolet radiation of 400 nm or less with a photopolymerization constituent, in the light source represented by the conventional high-pressure mercury-vapor lamp, it also had the problem that it did not harden.

[0007]The photo-curing in the case of many used the radical polymerization, and since the radical which is a start kind received oxygen inhibition, the oxygen interception film was required for it to obtain the hardened material of thickness of several microns or less.

[0008]In a long wavelength region, highly, exposure speed of photosensitivity is large without an oxygen interception film, and, moreover, the place which this invention was made paying attention to such a problem, and is made into the technical problem has it in providing a near visible photopolymerization nature constituent transparently and colorlessly after photo-curing.

[0009]

[Means for Solving the Problem]Then, by adding a certain specific photopolymerization initiator, as a result of repeating research wholeheartedly, in order that this invention persons may solve an aforementioned problem, It finds out that a photopolymerization nature constituent containing a compound in which cationic polymerization is possible carries out photopolymerization efficiently by the visible light exposure of not less than 400 nm, and comes to complete this invention.

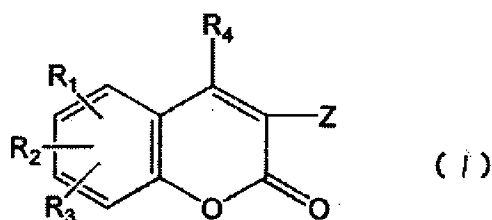
[0010]A compound which this invention is made that an aforementioned problem should be solved and has at least one or more substituents in which (A) cationic polymerization of the invention according to claim 1 is possible, (B) Aromatic onium salt which will generate Broensted acid or Lewis acid which activates cationic polymerization if chemical action radiation is exposed, (C) It is a visible photopolymerization nature constituent containing containing a compound which has the molecular structure which carried out conjugate to a dialkylamino group, and carries out sulfonic acid derivative generating of the aromatic onium salt (B) by operation of coloring matter in which spectral sensitization is possible, and (D) Broensted acid or Lewis acid.

[0011]In a visible photopolymerization nature constituent of claim 1 the invention according to claim 2, Exposure of chemical action radiation will be characterized by aromatic onium salt (B) which generates Broensted acid or Lewis acid which activates radical species which activate a radical polymerization, and cationic polymerization being diaryliodonium salt.

[0012]In the visible photopolymerization nature constituent according to claim 1 or 2, the invention according to claim 3 has the molecular structure which carried out conjugate to a dialkylamino group, and is characterized by being 3-substitution coumarin compound in which coloring matter (C) in which spectral sensitization is possible is shown with a following general formula (1) in aromatic onium salt (B).

[0013]

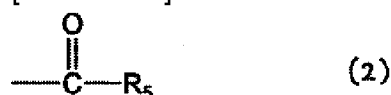
[Formula 5]



[0014] ( $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  may form a condensed ring system or a condensation heterocyclic system among a formula by hydrogen, an alkyl group, the alkoxy group, the alkylamino group, the dialkylamino group, a cyano group, or two.)  $Z$  shows an aryl group, a heterocycle group, or the basis expressed with a general formula (2).  $R_5$  shows an alkyl group, an alkoxy group, an aryl group, an aryloxy group, and a heterocycle group.

[0015]

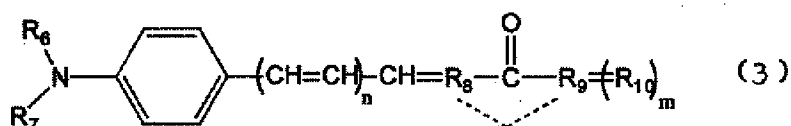
[Formula 6]



[0016] In the visible photopolymerization nature constituent according to claim 1 or 2, the invention according to claim 4 has the molecular structure which carried out conjugate to the dialkylamino group, and is characterized by being p-amino unsaturated ketone compound in which the coloring matter (C) in which spectral sensitization is possible is shown with a following general formula (3) in aromatic onium salt (B).

[0017]

[Formula 7]

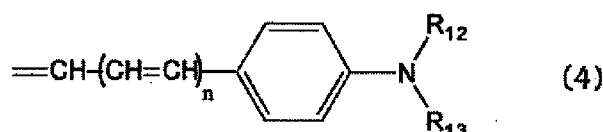


[0018] the inside of a formula,  $m$ , and  $n$  are 0 or 1, respectively --  $R_6$  and  $R_7$  -- an alkyl group with a hydrogen atom or 1-5 carbon atoms. or  $\text{CH}_2\text{COOR}_{11}$  (however,  $R_{11}$  -- a hydrogen atom or the alkyl group of 1-5 of a carbon number.) An alkaline metal, ammonium, and amine are shown or  $\text{C}_2\text{H}_4\text{CF}_3$ ,  $\text{C}_2\text{H}_4\text{I}$ ,  $\text{C}_2\text{H}_4\text{Br}$ ,  $\text{C}_2\text{H}_4\text{Cl}$ ,  $\text{C}_2\text{H}_4\text{F}$ ,  $\text{C}_2\text{H}_4\text{CN}$ , and  $\text{C}_2\text{H}_4\text{NO}_2$  is shown. An alkylene ylidene group with 1-5 carbon atoms which  $R_8$  can be combined with a methylidyne group or  $R_9$ , and can form a ring with a carbonyl group, The basis in which  $R_9$  forms indanone or tetralone with a carbon atom, a substituent, an unsubstituted group phenyl group, or  $R_8$  and a carbonyl group, the basis (however,  $R_{12}$  and  $R_{13}$  -- an alkyl group with a hydrogen atom or

1-5 carbon atoms.) expressed with a general formula (4) or  $\text{CH}_2\text{COOR}_{11}$  (however,  $\text{R}_{11}$  -- a hydrogen atom or the alkyl group of 1-5 of a carbon number.) An alkaline metal, ammonium, and amine are shown or they are  $\text{C}_2\text{H}_4\text{CF}_3$ ,  $\text{C}_2\text{H}_4\text{I}$ ,  $\text{C}_2\text{H}_4\text{Br}$ ,  $\text{C}_2\text{H}_4\text{Cl}$ ,  $\text{C}_2\text{H}_4\text{F}$ ,  $\text{C}_2\text{H}_4\text{CN}$ , and  $\text{C}_2\text{H}_4\text{NO}_2$ . It is shown.

[0019]

[Formula 8]



[0020]The invention according to claim 5 is (E) solvent fusibility in the visible photopolymerization nature constituent according to claim 1, 2, 3, or 4, And the compound which is a solid in ordinary temperature and ordinary pressure, and has at least one or more ethylenic unsaturated bonds in which the (A) radical polymerization is possible, and a polymer with compatibility are contained. [0021]

[Embodiment of the Invention]Hereafter, this invention is explained in detail.

[0022]As a compound which has at least one or more substituents which are used by this invention, and in which ingredient (A) cationic polymerization is possible, As for alicyclic epoxy groups, a glycidyl group, cyclic ether, an annular sulfide, annular imine, a cyclic disulfide, lactone, lactam, cyclic formal, annular imino ether, vinyl ether, etc., it is desirable in a structural unit at least one or to contain one or more.

[0023]As an example, diglycerol polyglycidyl ether, pentaerythritol polyglycidyl ether, 1,4-bis(2,3-epoxy propoxy perfluoro isopropyl)cyclohexane, Sorbitol PORIGURISHI gill box ether, trimethylolpropane polyglycidyl ether, 1, 6-hexanediol diglycidyl ether, resorcinol diglycidyl ether, Polyethylene glycol diglycidyl ether, phenyl glycidyl ether, p-tertiarybutyl phenyl glycidyl ether, adipic acid diglycidyl ester, Orthophthalic acid diglycidyl ester, dibromo phenyl glycidyl ether, Dibromoneopentylglycol diglycidyl ether, 1,2,7,8-diepoxy octane, 1,6-dimethylol perfluorohexane diglycidyl ether, 4,4'-bis(2,3-epoxy propoxy perfluoro isopropyl)diphenyl ether, The 3,4-epoxycyclohexylmethyl 3', 4'-epoxy cyclohexane carboxylate, 1,2,5,6-diepoxy-4,7-methano perhydro indene, 2-(3, 4-epoxycyclohexyl)-3', 4'-epoxy-1,3-dioxane 5-spirocyclohexane, A 1,2-ethylene dioxyscrew (3,4-epoxycyclohexyl methane), 4', 5'-epoxy-2'-methylcyclohexylmethyl-4,5-epoxy-2-methylcyclohexane carboxylate, An ethylene glycol screw (3,4-epoxy chrysanthemum ROHEKISANKARUKISHI rate), A bis-(3,4-epoxycyclohexylmethyl) horse mackerel peat, di-2,3-epoxy cyclopentylether, Vinyl-2-chloroethyl ether, vinyl-n-butyl

ether, Triethylene glycol divinyl ether, 1,4-cyclohexane methanol divinyl ether, Trimethylolmethane TORIBINIRU ether vinyl glycidyl ether, 1,3-screw [-- 2- (3[-- 7-oxabicyclo [4.1.0] -- a PUCHIRU] ethyl] siloxane.) 3,3 - a screw -- [-- [-- dimethyl -- [-- two (it is \*\*\*\*- 3-yl to 7-oxabicyclo [4.1.0]) -- ethyl --] -- silyl --] -- oxy --] -1,1,5,5 - tetramethyl one -- 1,5 - a screw -- [- two - (it is \*\*\*\*- 3-yl to 7-oxabicyclo [4.1.0]) -- ethyl --] -- trisiloxane. Arda Ito CY175, CY177, It is also possible to use two or more kinds depending on CY179, CY184, and CY192 (made by Ciba-Geigy) these uses, combining.

[0024]As a photoinitiator system which will activate cationic polymerization if it exposes in the ingredient (B) chemical action radiation of this invention, BURENSUTTEDO acid or Lewis acid is simultaneously generated by optical exposure. As this aromatic onium salt, a diphenyliodonium salt etc. are preferred. As that of a diphenyliodonium salt which is used by this invention, Macromolecules, 10, a compound given in 1307(1977)., For example, diphenyliodonium, ditolyl iodonium, phenyl (p-anisyl) iodonium, Bis(m-nitrophenyl)iodonium, bis(p-t-buthylphenyl)iodonium, Chloride of iodonium, such as bis(p-chlorophenyl)iodonium, Although bromide or tetrafluoroborate, a tetrakis (pentafluoro phenyl) borate salt, a hexafluorophosphate salt, a hexafluoroarsenate salt, etc. can be mentioned, it is not limited to these.

[0025]As a 3-substitution coumarin compound shown by said general formula (1) which is an ingredient (C) of this invention, Specifically, it is the 7-diethylamino 3. -(2-benzo thiazyl)- Coumarin, 7-diethylamino 3 -(2-benzo imidazolyl)- Coumarin, A 7-diethylamino 3-benzoylcoumarin, a 7-diethylamino 3-thieno yl coumarin, A 7-diethylamino 3,3'-carbonyl bisque marine \*\*3,3'-carbonyl screw (7-diethylamino coumarin), Although a 9,9'-carbonyl screw (1,2,4,5-tetrahydro 3 H,6 H,10H [I] benzo PIRANO [ 9,9 a,1-] [gh] kino \*\*\*\*\*- 10-one) etc. can be mentioned, it is not limited to these. The synthesizing method of these compounds is indicated to Chemical Reviews 361 (1945) and Tetrahedron 38(9)1203-1211 (1982).

[0026]As a p-aminophenyl unsaturated ketone compound shown by said general formula (3) which is an ingredient (C) of this invention, Specifically 2,5-bis(4'-diethylamino benzyliene) cyclopentanone, 2,5-bis(4'-dimethylamino benzyliene)cyclopentanone, 2,6-bis(4'-diethylamino benzyliene)cyclohexanone, 2,6-bis(4'-dimethylamino benzyliene)cyclohexanone, 2,5-bis(4'-dimethylamino thinner MIRIDEN)cyclopentanone, 2,6-bis(4'-dimethylamino thinner MIRIDEN) cyclohexanone, 1,3-bis(4'-dimethylamino benzyliene)acetone, 2-(4'-diethylamino benzyliene)-1-inda non, 2-(9'-JURORIRIDEN)-1-inda non, 2-(4'-diethylamino benzyliene)-1-tetralone, A 4'-diethylamino 2'-methylbenzyliene-acetophenone, 2,5-bis(4'-N-ethyl-N-carbomethoxy methylamino benzyliene)cyclopentanone and its sodium salt, 2,5-bis(4'-N-methyl-N-cyano ethylamino benzyliene)cyclopentanone, 2,5-bis(4'-N-ethyl-N-KURORU ethylamino thinner MIRIDEN)cyclopentanone, 2,6-bis(4'-N-cyano ethylamino benzyliene)cyclohexanone, 2-(4'-N-ethyl-N-carboxy methylamino benzyliene)-1-inda non, Although 2-(4'-N-ethyl-N-carboxy

methylamino benzyliene)-1-tetralone, 2-(4'-ethyl-N-cyano ethylamino benzyliene)-1-indanone, its sodium salt, etc. can be mentioned, it is not limited to these. moreover -- these sensitizing dye can be chosen so that the wavelength of the radiant ray which serves as a light source by the purpose of use may be suited -- a use -- two or more kinds -- you may combine and use it.

[0027]As a compound which generates a sulfonic acid derivative by operation of the Lewis acid or Brønsted acid which is an ingredient (D) of this invention, P-toluenesulfonic-acid ester and methanesulfonate ester \*\* which are obtained by a reaction with the compound of various kinds of alcohol, p-tosylchloride, or methanesulfonyl chloride can be mentioned. Specifically 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butylester, 2-methyl-2-methanesulfonyloxy 3-keto butanoic acid tert butylester, 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid 2-phenyl-2 \*\*PURO pill ester, 2 - Methyl-2-methanesulfonyloxy 3-keto butanoic acid 2-phenyl-2 \*\*PURO pill ester, \*\*\*\*- 1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane, Although there are 1,2-epoxy-2-methyl-3-(p-toluenesulfonyloxy) propane, 1-(p-toluenesulfonyloxy)-3-phenyl-3,3-ethylene dioxyp propane, etc., it is not limited to these. These can be combined with two or more kinds of arbitration, and can be used for this invention.

[0028]The compound which has at least one or more ethylenic unsaturated bonds in which a radical polymerization is possible as a polymer which is an ingredient (E) of this invention, and the thing which has compatibility must be chosen. As long as it is a compound which has at least one or more ethylenic unsaturated bonds in which a radical polymerization is possible, and line organic polymer with compatibility, there is no restriction in particular, but. Specifically Polyacrylates and Poly alpha-alkyl acrylate. Polyamide, polyvinyl acetals, polyurethane, and polycarbonate. Thermoplastics which is represented by polystyrene, polyvinyl ester species, etc., Although thermosetting resin which is represented by various epoxy resins, such as bisphenol A and bisphenol A D, the bisphenol B, bisphenol A F, the bisphenol S, novolac, o-cresolnovolac, and p-acrylic phenol novolac, is mentioned, It is not limited to these. It is also possible to mix two or more kinds of thermoplastics and thermosetting resin which are solids if needed, and to apply in ordinary temperature and ordinary pressure, by such solvent fusibility. What is necessary is just to use a polymer which dissolves or swells in water or weak alkali solution, when the visible photopolymerization constituent especially applied to this invention is applied to manufacture of photosensitive printing plates, surface relief type holograms, etc. As such a polymer, the copolymer which carries out adequate amount content of the carboxylic acid, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, and crotonic acid, is mentioned to a side chain.

[0029]In painting the visible photopolymerization constituent of this invention on a base material, For example, toluene, xylene, chlorobenzene, chloroform, a dichloroethane, A dichloroethylene, trichloroethylene, methyl isobutyl ketone, Dioxane, a tetrahydrofuran, isopropanol, n-butanol, 2-methoxyethanol, 2-methoxy ethyl acetate, propylene glycol

monomethyl ether, It can be made to be able to dissolve in the mixed solvent which was independent as for suitable solvents, such as 3-methoxy propanol, 3-methoxy propyl acetate, methyl ethyl ketone, and acetone, or combined these suitably, and can use.

[0030]To the visible photopolymerization constituent of this invention, in order to solve various problems on practical use, it is still more possible to use various additive agents together. For example, the purpose of promoting addition of thermal polymerization inhibitor, such as p-methoxy phenol, hydroquinone, catechol, and phenothiazin, and a polymerization in order to prevent the thermal polymerization at the time of preservation. Addition of addition of chain transfer agents, such as amine, a thiol, and disulfide, or a defoaming agent, a leveling agent, a plasticizer, an antioxidant, fire retardant, a spray for preventing static electricity, an antihalation agent, etc. is possible.

[0031]The sensitizing solution which chose each of these ingredients suitably, and was mixed and obtained at an arbitrary rate Thus, a spin coater, Publicly known coating means, such as a roll coater, a bar coating machine, and a dispenser, are used, it substrate-applies, or it is dropped and a glass plate, a polycarbonate board, a polymethylmethacrylate board, polyester film, etc. use. The visible photopolymerization constituent concerning this invention A carbon arc lamp, a metal halide lamp, It has good sensitivity to the light source which has a source of an oscillation in a near infrared field (400-650 nm) from light ranges, such as xenon light, a high-pressure mercury-vapor lamp, argon laser, helium cadmium laser, krypton laser, He Ne laser, SHG laser, and a semiconductor laser.

[0032]Although the mechanism of a polymerization start is not necessarily clear as a principle of this invention, It is thought that the electronic transition from the sensitizing dye which is the molecule characteristic top electronic receptiveness, and was excited to onium salt arises, an aryl (or alkyl) radical is split, and the onium salt used in this invention functions as a polymerization start kind. That is, it is thought that the thing which are depended on an electron release reaction by optical exposure and which free radical generating is carried out and Lewis acid or Broensted acid functions as a photopolymerization initiator as a result becomes possible. It is made to decolorize with the sulfonic acid which generated the sensitizing dye which became unnecessary after photo-curing from the compound which generates sulfonic acid with said Lewis acid by which it was generated, or Broensted acid. With the sulfonic acid generated by giving this operation to the compound which generates the sulfonic acid derivative beforehand contained among material, the sensitizing dye required in order to obtain a hardened material reacts to the amino group of this sensitizing dye, and is formed into 4 class, The function as an auxochrome is lost, and in order for the absorption wavelength region of this coloring matter to carry out a short wavelength shift and to move to an ultraviolet area, I think that decolorization in a light region takes place. This sensitizing dye that the amino group formed into 4 class is excellent in weatherability including heat, and coloring by



decomposition etc. does not take place in the preservation over a long period of time.

[0033]

[Example] Hereafter, a concrete example explains this invention still in detail.

The 2-methyl-3-keto butanoic acid tert-butylester which obtained it under existence of tetrahydrofuran Nakamizu[Shiroshi]-ized sodium by making <Example 1> acetoacetic acid tert-butylester react to a methyl iodide was made to react to formalin under existence of ethanol Nakamizu[Shiroshi]-ized sodium. The generated 2-hydroxymethyl-3-keto butanoic acid tert-butylester is made to react to p-tosyl chloride under the triethylamine existence in dichloromethane, 2-methyl-2(p-toluenesulfonyloxy)-3-keto butanoic acid tert-butylester was obtained.

[0034] Alicyclic epoxy compound CY-179 (made by Ciba-Geigy) 100 weight section, Bis(tert-butylphenyl)iodonium hexafluorophosphate 5 weight section, 3,3'-carbonyl bis(7-diethylamino coumarin) 0.25 weight section, After stirring the mixture of 2-methyl-2(p-toluenesulfonyloxy)-3-keto butanoic acid tert-butylester 5 weight section until it became uniform, it applied so that the thickness might be set to about 5 micrometers on a glass substrate.

[0035] Next, the xenon light of 500W was used for the light source, and it irradiated with the visible light obtained through the cut-off filter [Toshiba Glass company make trade name: Y-43] to the coat on the above-mentioned glass substrate, and was considered as sensitivity in quest of exposure time until the coat surface becomes a tack freelaner using talc powder. The transmissivity of 400-600 nm was measured for the film surface stiffened on the same conditions by Shimadzu spectrophotometer UV-160A. A result is shown in Table 1.

[0036] The result operated like Example 1 is shown in Table 1 except using the following instead of the aromatic onium salt of <Example 2-8> example 1, and sensitizing dye.

[0037]

[Table 1]

実施例	芳香族 オニウム塩	増感色素	硬化時間 (sec)	透過率 (%)
1	O-1	D-1	16	85
2	O-1	D-2	20	83
3	O-1	D-3	22	86
4	O-1	D-4	18	82
5	O-1	D-5	24	82
6	O-1	D-6	21	85
7	O-2	D-1	19	83
8	O-3	D-1	12	81

[0038]

O-1; A screw. (p-tert buthylphenyl) Iodonium hexafluorophosphate O-2; A diphenyliodonium tetrafluoroborate O-3;4-octyloxy phenyl (phenyl) iodonium hexafluoroantimonate D-1;3,3'-carbonyl screw. (7-diethylamino coumarin)

D-2;7-diethylamino 3-. (2-benzo imidazolyl) Coumarin D-3;2,5-screw [[4-(diethylamino) phenyl] Methylene]-cyclopentanone D-4;2-benzoyl-3-(p-dimethylaminophenyl)-2-propene nitril D-5;4-. (p-dimethylaminophenyl)-1,3-butadienyl p-methoxyphenone D-6;2-(p-dimethylaminophenyl) ethenyl-p-methoxyphenone [0039]In <Examples 9-16> example 1, except using methanesulfonyl chloride instead of p-tosyl chloride, and using 2-methyl-2 methane-sulfonyloxy 3-keto butanoic acid tert-butylester, it was operated like Example 1 and the hardened material was obtained. A result is shown in Table 2.

[0040]

[Table 2]

実施例	芳香族 オニウム塩	増感色素	硬化時間 (sec)	透過率 (%)
9	O-1	D-1	16	83
10	O-1	D-2	21	82
11	O-1	D-3	21	84
12	O-1	D-4	17	82
13	O-1	D-5	25	81
14	O-1	D-6	20	80
15	O-2	D-1	18	82
16	O-3	D-1	13	80

[0041]Instead of compound CY-179 (made by Ciba-Geigy) which has at least one or more substituents in which cationic polymerization is possible in <Example 17-19> example 1, the result operated like Example 1 is shown in Table 3 except using the following compounds.

[0042]

[Table 3]

実施例	カチオン重合性 化合物	硬化時間 (sec)	透過率 (%)
17	M-1	20	87
18	M-2	25	85
19	M-3	22	86

[0043]

M-1; dibromo phenyl-glycidyl-ether M-2;1,3-screw [2 - (it is PUCHIRU) ethyl] siloxane M-3;CY-175 to 3[7-oxabicyclo [4.1.0]] [0044]<Example 20> alicyclic epoxy compound CY-179 (made

by Ciba-Geigy) 100 weight section, Bis(tert-buthylphenyl)iodonium hexafluorophosphate 5 weight section, 3,3'-carbonyl bis(7-diethylamino coumarin)0.25 weight section, 2-methyl-2(p-toluenesulfonyloxy)-3-keto butanoic acid tert-butylester 5 weight section, The liquid which carried out the mixture solution of the KISHIRU acrylate methyl methacrylate copolymer 100 weight section to methyl-ethyl-ketone 200 weight section to 2-ethyl which refined by performing a radical polymerization in accordance with the conventional method is applied so that a spin coater may be used and the dry membrane thickness may be set to about 2 micrometers on an anodized aluminium board, It was made to dry for 2 minutes at 70 \*\* with a dryer, and the photosensitive layer was formed.

[0045]The sensitivity to the visible light of each obtained sensitive plate was measured as follows. Namely, a step tablet (Kodak trade name step tablet No.2) is stuck on a photosensitive resin composition test panel (sensitive plate concerning each example), After irradiating with the light by 514.5-nm argon laser from besides, negatives were developed in 0.1% of sodium hydroxide solution, and it asked by calculating the light volume of the visible light which hardening of a photosensitive layer takes from that hardening number of stages. This result is shown in Table 4.

[0046]The result operated like Example 20 is shown in Table 4 except using the following instead of the aromatic onium salt of <Example 21-27> example 20, and sensitizing dye.

[0047]

[Table 4]

実施例	芳香族 オニウム塩	増感色素	硬化時間 (sec)	透過率 (%)
20	O-1	D-1	10	89
21	O-1	D-2	15	86
22	O-1	D-3	16	89
23	O-1	D-4	14	87
24	O-1	D-5	19	85
25	O-1	D-6	18	89
26	O-2	D-1	15	86
27	O-3	D-1	9	86

[0048]The <comparative example 1-4> sulfonic acid generating agent is not added, but the result operated like Examples 1 and 5 is shown in Table 5 except changing the amount of sensitizing dye.

[0049]

[Table 5]

比較例	芳香族 オニウム塩	増感色素	硬化時間 (sec)	透過率 (%)
1	O-1	D-1	18	71
2	O-1	D-5	24	65

[0050][Check] In order to obtain a water-white hardened material so that clearly from the data of the transmissivity after hardening of the visible photopolymerization constituent concerning the comparative examples 1-2, it was checked that an improvement cannot be aimed at unless it adds a sulfonic acid generating agent.

[0051]

[Effect of the Invention]According to the visible photopolymerization nature constituent concerning this invention, aromatic onium salt, sensitizing dye, And while having photosensitivity in a not less than 400-nm long wavelength region and being able to aim at improvement in the exposure speed by having applied the compound which carries out sulfonic acid derivative generating by operation of Broensted acid or Lewis acid, a near hardened material is obtained transparently and colorlessly.

[0052]Therefore, it has an effect applicable as recording materials, such as the printing plate for laser direct, a printed circuit board, an optical disc, optical memory, a hologram, and photoresist, or photo-curing type adhesives.

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[Translation done.]